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(6) THERMAL PROPERTIES OF ALLOYS
AT HIGH TEMPERATURES

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(10) by

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INTRODUCTION

Although high temperature heat capacities and heat contents of a large number of inorganic compounds have been extensively measured, corresponding thermal data for metallic alloys are quite scarce. The need for such data in studies of alloy thermochemistry is twofold. First, knowledge of the heat capacity of an alloy is necessary if values of other thermodynamic properties, such as heat, entropy, or free energy of formation, measured at a single temperature, are to be extended to other temperatures of interest. In the absence of actual data such extrapolations are usually accomplished through the assumption of Kopp's Law, i. e., that the heat capacity of the alloy is the sum of the heat capacities of the components, or stated quantitatively, that $\Delta Cp = 0$ and ΔH and ΔS are invariant with temperature for the formation of the alloy. This assumption represents a limiting type of behavior which is probably not valid for the large majority of alloy phases.

Secondly, accurate heat capacity data for alloys are of interest in themselves in studies of many phenomena characteristic of alloys and thus contribute to knowledge of alloy crystal chemistry and interatomic bonding theory. Among the mechanisms of energy absorption with rising temperature which may contribute to the total heat capacity and which may be studied by analyses of heat capacity data may be listed the following:

1. Harmonic lattice vibrations
2. Anharmonic lattice vibrations
3. Electronic energy absorption
4. Dilation ($Cp - Cv$)

5. Destruction of ferromagnetism

6. Destruction of antiferromagnetism

7. Destruction of long-range order

8. Destruction of short-range order

9. Destruction of clustering of like atoms

Heat content data may serve to determine heats of transformation where changes in crystal structure or phase are involved. Precise knowledge of heat capacity behavior in regions just above and just below the transition temperature is especially significant in considerations of phase transformation theories. Many of the significant aspects of heat capacity behavior have been discussed in Technical Note No. 4.[4*]

The objectives of this investigation ~~have been~~ were to determine the high temperature thermal properties of various representative alloy systems from heat content measurements, to examine the validity of Kopp's Law of additivity of heat capacities of the components, and where possible to correlate the data with various aspects of atomic bonding phenomena in alloys. Heat contents also were measured for a number of pure metals for which existing data were either incomplete or uncertain.

This report reviews briefly the accomplishments of this project, referring where possible to the published papers and technical notes ~~which have been~~ previously submitted. Copies of Technical Note No. 7 and of the most recent publication resulting from this project are ~~being~~ submitted as part of this report.

* Superscript reference numbers refer to the published papers, technical notes, and associated references resulting from this project which are listed at the end of this report.

RESULTS OF RESEARCH

HIGH TEMPERATURE HEAT CONTENT CALORIMETER

A high-temperature calorimeter operating on the principle of the Bunsen ice calorimeter but using diphenyl ether as the working substance has been developed and used for making the heat content measurements. It operates at a more convenient temperature (27°C) and has greater sensitivity than the ice calorimeter. Heat contents with respect to 298°K are determined at temperatures up to 1450°K with an average precision of about ± 0.3 %. The measurements are rapid and require a minimum of calculation and correction. Descriptions of the apparatus and experimental techniques have been published.[3, 8]

HEAT CONTENT DATA FOR PURE METALS

During the course of the investigations, heat contents, $H^o_T - H^o_{298}$, have been measured and the other thermal properties, Cp, $S^o_T - S^o_{298}$, and $F^o_T - H^o_{298} / T$, have been evaluated for a number of pure metals. Measurements for some of these metals, namely Ag, Al, Au, Bi, Cu, Ni, Pb, Pd, and Si, have been made primarily to obtain data from the same apparatus for the pure components as for the binary alloys which were studied. This was necessary to eliminate systematic errors which might have arisen in calculating Kopp's Law deviations for the alloys. Data for any of this group of elements which have not already been included in previous reports or publications dealing with the alloys studied will be given in future publications.

Measurements for a second group of metals, Cr, Fe, Hf, Pt, and Tl, were made to resolve uncertainties in previously existing data, or to obtain accurate thermal properties where none had existed. These data, which contribute significantly to knowledge of the thermodynamic properties of the elements, either have been or will be reported in separate publications, and are discussed briefly below.

Chromium (Cr). Heat contents were measured for a sample of high purity, oxygen-free, vapor deposited Cr from 345° to 1500°K. Previous reliable data for pure Cr (L. P. Armstrong and H. Grayson-Smith, Can. J. Research, 28A, 51, 1950) extended to only 1073°K. The data found agree with those of Armstrong and Grayson-Smith and extend the values to higher temperatures.

Iron (Fe). Heat contents of extremely pure Fe were measured over the range 338° to 1433°K. Results from three samples containing widely differing impurities agreed with one another and with previously reported results at higher temperatures, 1184° to 1809°K (M. Olette and A. Ferrier, Phys. Chem. Metallic Solns., Nat. Phys. Lab., Symposium No. 9, Vol. 1, Paper 4H, H. M. S. O., London, 11 pp., 1959). From these data tables of the thermodynamic functions of Fe at elevated temperatures have been prepared which are believed to be more accurate than any previously available. Cp values have been derived which are consistent with the heat content data, with the best experimental Cp data, and with the thermodynamic conditions of equilibrium between bcc and fcc iron. This study was the subject of a recent publication.[6]

Hafnium (Hf). No previous heat content data for this metal have been published probably due to the lack, until recently, of Hf metal of sufficient purity. Heat content measurements in the range from 339° to 1346°K have just been completed on a sample of Hf in which the only significant impurity is Zr, for which a reliable correction to the data can be made. The high-temperature thermal properties of Hf have been evaluated from the data, and a paper describing the results is in the final stages of preparation for submission to the Journal of Chemical and Engineering Data.

Platinum (Pt). The use of Pt as a secondary standard for calibrating high-temperature calorimeters makes it desirable to specify the heat contents of this metal as accurately and precisely as possible. Data obtained between 339° and 1435° K were combined with previously reported values, making possible the selection of thermodynamic properties of Pt which are thought to be more reliable and self-consistent than those of previous tabulations. Reprints of the publication[8] giving the results are included with this report.

Thallium (Tl). Measured heat content data for Tl (336° - 562° K) have permitted the selection of reliable thermal properties for α- and β-Tl, which was not possible from the data reported from a number of prior investigations which disagreed widely.

HEAT CONTENT DATA FOR BINARY ALLOYS

Fe Alloys. Heat contents for a number of binary Fe alloys, $Co_{.309}Fe_{.691}$, $Cr_{.094}Fe_{.906}$, $Cr_{.784}Fe_{.216}$, $Fe_{.696}Mn_{.304}$, $Fe_{.512}Mn_{.488}$, and $Fe_{.880}Si_{.120}$, were measured in the range from 350° to 1400° K. Values of $H_T - H_{298}$, $S_T - S_{298}$, Cp, and the Kopp's Law deviation, ΔCp, were evaluated and interpreted in terms of the magnetic characteristics of the alloys. An anomaly, possibly an antiferromagnetic transformation, was discovered at 517° K in $Fe_{.512}Mn_{.488}$ and at 380° K in $Fe_{.696}Mn_{.304}$. The results of this study have been submitted as a Technical Note[2] and have also been published.[6]

Al Alloys. Heat contents of the following binary Al alloys were measured, and the other thermal properties calculated, over the indicated temperature ranges:

$Ag_{.667}Al_{.333}$	352° - 973°K
$Al_{.472}Co_{.528}$	347° - 1413°K
$Al_{.108}Fe_{.892}$	351° - 1401°K
$Al_{.488}Fe_{.512}$	350° - 1410°K
$Al_{.484}Ni_{.516}$	351° - 1402°K

Three of these alloys, $Al_{.472}Co_{.528}$, $Al_{.488}Fe_{.512}$, and $Al_{.484}Ni_{.516}$, have the ordered bcc CsCl type superlattice structure and have highly exothermic heats of formation. All of these alloys were found to show similar substantial negative deviations from Kopp's Law, even after allowances are made for the magnetic anomalies in Fe and Ni, which, of course, make a large negative contribution to ΔCp for those alloys. The alloy $Al_{.108}Fe_{.892}$, however, which closely resembles pure Fe in magnetic behavior, was found to follow Kopp's Law closely. For the alloy $Ag_{.667}Al_{.333}$, ΔCp was found to increase from a slight negative value at 298°K to significant positive values at intermediate temperatures of measurement, and then to decrease again to negative values at higher temperatures. This behavior might well arise from the destruction of short range order with increasing temperature, which has been indicated by other studies on the mechanical properties of this alloy.

The results of this study will be presented in a future publication.

Extensive Solid Solution Alloys. Heat content measurements were made and the other thermal properties evaluated for the following alloys, all from completely miscible systems or from extensive terminal solubility regions:

$Ag_{.70}Au_{.30}$	346° - 1185°K
$Ag_{.50}Au_{.50}$	342° - 1185°K

conducted in this laboratory.[9] The Cp data enabled heats of formation, measured at 330°K, to be transferred to a temperature of 1000°K, where free energies had been reported, permitting calculation of the entropies of formation of the alloys.

The thermal properties of this group of alloys will be reported in a future publication.

Au-Zn Alloys. Heat contents of two Au-Zn alloys, α_2 (Au_3Zn), from 399° to 500°K, and β' (AuZn), from 399° to 898°K, were measured in connection with another thermodynamic study of these alloys.[10] Au_3Zn was found to obey Kopp's Law, but AuZn, which has an ordered bcc CsCl-type structure and a highly exothermic heat of formation, showed a negative deviation such as was found with AlFe, AlCo, and AlNi. As this deviation is opposite in sign to the effect from possible disordering of the β' phase during heating, it seems established that β' remains fully ordered to at least 900°K, in agreement with X-ray diffraction studies.

Bi-Pb Alloys. Heat contents were measured for four solid alloys from the Bi-Pb system from 385° to 485°K. The results, which show the alloys to obey Kopp's Law, were reported in a paper describing an extensive study of the thermodynamics of the Bi-Pb alloy system.[11]

Cr-Ni Alloys. Heat contents of four Ni-rich Cr-Ni alloys were determined between 400° and 1500°K. Aside from ferromagnetic effects, Kopp's Law of additivity was approximately followed with only slight positive deviations being found. The results appear to invalidate the previous results of A. W. Foster (Phil. Mag., 18, 470, 1934), who reported large negative deviations for dilute alloys of Cr in Ni. This study has been published.[1]

Cu-Zn Alloys - Study of Dilation Contribution to Heat Capacity. The dilational contribution to the heat capacity of Cu and α-brass was studied as a function of temperature and composition. In order to evaluate (Cp - Cv) it was necessary to determine the isothermal compressibilities of these materials. This was done by measuring the velocity of sound in Cu and the α-brasses by means of the ultrasonic pulse technique. Measurements were made between 77° and 800°K. Heat contents were also measured between 300° and 800°K. An attempt was made to analyze the data for the separate contributions to the total heat capacity. This work is described in Technical Note No. 7[7] which is being submitted as part of this report.

FUTURE WORK

The apparatus and techniques perfected with the aid of support from the U.S. Air Force Office of Scientific Research will continue to be used in future studies. A larger calorimeter, identical in principle with the one now in operation but allowing measurements to be made on samples enclosed in sealed containers, is being assembled. This new instrument will permit studies to be made on materials which might react with the atmosphere or have appreciable vapor pressures and on liquids as well as solids. Measurements are now being planned for a series of the so-called III-V intermetallic compounds. The work is being continued under the sponsorship of the Atomic Energy Commission, through the recently established Inorganic Materials Research Division of the Lawrence Radiation Laboratory.

PUBLISHED PAPERS AND TECHNICAL NOTES RESULTING FROM WORK PERFORMED UNDER CONTRACT NO. AF 49(638)-83

1. "The Heat Capacity of Dilute Solutions of Chromium in Nickel," Ralph Hultgren and Cletis Land, Trans. Met. Soc. AIME, 215, 165 (1959). Reprints submitted as Technical Note No. 1, July, 1959.

2. "High Temperature Heat Contents of Some Binary Iron Alloys," Weston B. Kendall, Raymond L. Orr, and Ralph Hultgren, Technical Note No. 2, July, 1959.

3. "A Diphenyl Ether Calorimeter for Measuring High Temperature Heat Contents of Metals and Alloys," Ralph Hultgren, Peter Newcomb, Raymond L. Orr, and Linda Warner, Phys. Chem. Metallic Solns., Natl. Phys. Lab., Symposium No. 9, Vol. 1, Paper 1H, H.M.S.O., London, 8 pp. (1959). Reprints submitted as Technical Note No. 3, March, 1960.

4. "Specific Heat of Metals and Alloys," (Lecture given at Third Annual Conference, March 29, 1960, Thermochemical Properties Research Center, Purdue University), Ralph Hultgren, Technical Note No. 4, June, 1960.

5. "High Temperature Heat Contents of Some Binary Iron Alloys," W. B. Kendall and Ralph Hultgren, Trans. ASM, 53, 207 (1961). Reprints submitted as Technical Note No. 5, March, 1961.

6. "The Thermodynamics of Solid Iron at Elevated Temperatures," Philip D. Anderson and Ralph Hultgren, Trans. Met. Soc. AIME, 224, 842 (1962). Reprints submitted as Technical Note No. 6, October, 1962.

7. "Dilation Contribution to Heat Capacity of Metals and Alloys," Yong-Shan Austin Chang and Ralph Hultgren, Technical Note No. 7, January, 1963. Copies being submitted with this report.

8. "Heat Content of Platinum," W. B. Kendall, R. L. Orr, and Ralph Hultgren, Jour. Chem. and Engr. Data, 7, 516 (1962). Reprints being submitted with this report.

ASSOCIATED REFERENCES PERTAINING TO PROJECT WORK

9. "The Heats of Formation of Silver-Palladium Alloys," John P. Chan, Philip D. Anderson, Raymond L. Orr, and Ralph Hultgren, Technical Report No. 4, Contract No. DA-04-200-ORD-171, T.O. No. 15, Materials Research Laboratory, University of California, October 1, 1959.

10. "Heats of Formation of Au_3Zn and AuZn," Ray W. Carpenter, Raymond L. Orr, and Ralph Hultgren, Technical Report No. 3, Contract No. DA-04-200-ORD-171, T.O. No. 15, Materials Research Laboratory, University of California, October 1, 1959.

11. "The Thermodynamics of Bismuth-Lead Alloys," P. Roy, R. L. Orr, and Ralph Hultgren, J. Phys. Chem., 64, 1034 (1960).

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